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TRANSLATION FROM JAPANESE

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(54) Title of the Invention: **Electrolyte Diaphragm**

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(65) Japanese Laid-Open Patent Application No. 61-246394
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Judicial Panel: Makoto Nagase, Chief Judge, Kiyo Nakajima, Judge, Mitsuo Suma, Judge
(56) Cited Publications: Japanese Laid-Open Patent Application 56-63770 (JP,A)

(57) Claims

1 An electrolyte diaphragm, characterized by the fact that a polytetrafluoroethylene film with a porosity of 35% or higher comprising innumerable fibrils formed between a plurality of microscopic nodes by drawing is uniformly impregnated and united with a perfluoro ion exchange resin, [the product of which is] molded to a thickness of 20 to 50 μm.

Detailed Description of the Invention

Object of the Invention

The present invention relates to an electrolyte diaphragm, and offers a product that has low resistance and enhanced coulomb efficiency as an electrolyte diaphragm in halogen-zinc cells, alkaline cells, and the like; that has excellent dimensional stability in cell liquids; and that has excellent mechanical strength even under dry conditions.

Field of Industrial Utilization

Electrolyte diaphragm in halogen-zinc cells, alkaline cells, and the like.

Prior Art

Films made from ion exchange resins are known and are used conventionally as separators in halogen-zinc cells, alkaline cells, and the like. Films of cellophane and other microporous natural macromolecular films, plastic films graft polymerized with acrylic acid or methacrylic acid are also known.

Further, Japanese Laid-Open Patent Application 56-63770 discloses a porous film impregnated and united with an ion exchange resin. Japanese Laid-Open Patent Application 52-114710 discloses a method for manufacturing a polytetrafluoroethylene-blended paper; particularly when the blended paper produced by this manufacturing method contains a hydrophilic solid particulate such as silica, it possesses uniform hydrophilic properties extending to the interior and swells in water, allowing it to be used as an electrolyte diaphragm.

Problems Which the Invention Is Intended to Solve

However, conventional products of the type described above have various drawbacks. Films made from ion exchange resins have the advantage that oxidants and other such substances do not penetrate; however, attempts to produce thin films or to

raise exchange capacity impair strength, dimensional stability in liquids, and the like, reduce mechanical strength and increase susceptibility to cracking in the dry state, and results in extreme swelling when the product contains water. These undesirable phenomenon reduce electrical resistance, and are particularly pronounced when the film has been thinned with the aim of raising coulomb efficiency, resulting in poor workability in most cases.

With products consisting of microporous natural macromolecular films, oxidation and deterioration induced by manganese dioxide and other oxidants used for the anode is severe. With plastic films graft-polymerized with acrylic acid or the like, electrical resistance is low, but the anode active material diffuses towards the counter electrode, shortening cell life. In the case of halogen-zinc cell diaphragms in particular, halogen self-discharge rises and coulomb efficiency is reduced, and the zinc halide, used in dissolved form, produces severe corrosion.

Structure of the Invention

Means Used to Solve the Aforementioned Problems

An electrolyte diaphragm, characterized by the fact that a polytetrafluoroethylene film with a porosity of 35% or higher comprising innumerable fibrils between a plurality of microscopic nodes formed by drawing is impregnated uniformly and united with a perfluoro ion exchange resin, producing a thickness of 20 to 50 μm.

Effect of the Invention

The use of a polytetrafluoroethylene film comprising innumerable fibrils between a plurality of microscopic nodes formed by drawing affords mechanical strength when dry and dimensional stability in liquid, and provides a stable electrolyte diaphragm.

The porosity of the aforementioned polytetrafluoroethylene film is at least 35% so that the perfluoro ion exchange resin suitably penetrates and becomes united with the texture of the film.

The thickness of the aforementioned polytetrafluoroethylene film which the perfluoro ion exchange resin has penetrated and become united is 20 to 50 μm so that electrolyte diaphragm function is preserved, electrical resistance is lowered, and coulomb efficiency is kept high.

Active substance diffusion can be regulated by adjusting the amount of impregnated, combined ion exchange resin to adjust the specific gravity of the polytetrafluoroethylene film.

Practical Examples

Specific embodiments of the present invention will be described referring to the appended drawings*. The product afforded in the present invention is a polytetrafluoroethylene (hereinafter PTFE) resin film with a porosity of 35% or higher, and preferably 40% or higher, uniformly impregnated and united with a perfluoro ion exchange resin.

Specific methods for uniformly bonding and uniting the aforementioned PTFE film and perfluoro ion exchange resin include any of the following:
(1) Thorough impregnation of a porous PTFE film (obtained by drawing) with a perfluoro ion exchange resin solution to produce a compact diaphragm.
(2) Impregnation with a perfluoro ion exchange resin as in (1) but in an incomplete manner to produce a porous diaphragm.
(3) Additional lamination and unification of the product of (1) or (2) with a perfluoro ion exchange resin.

In any case, the proportion of the perfluoro ion exchange resin with respect to the PTFE is preferably 3 to 90%, and particularly 10 to 30%, by weight ratio. The diaphragm thickness is 20 to 50 μm.

When the diaphragm obtained in the foregoing manner is used as a separator in a halogen-zinc cell, the fact that the product is formed with a PTFE film as a substrate affords excellent mechanical strength and dimensional stability even when thin, and the fact that it is perfluoro-based means that it does not experience deterioration due to the electrolyte. Electrolytic resistance is low and coulomb efficiency is excellent. Cell life is also significantly increased relative to conventional microporous natural macromolecular films, and performance is greatly improved.

The same holds true when the product is used as a separator for alkaline cells. Since electrical resistance can be lowered by the use of thin layers, as noted above, the capability of preventing diffusion of the anode active material to the counter electrode is excellent, afford a favorable product.

* [Translator's note: There are no drawings provided in the original.]

A specific example of manufacture of the product which pertains to the present invention is described below.

A porous PTFE film material conferred by drawing with innumerable fibrils located between microscopic nodes like a spider web and having a thickness of 25 μm and a porosity of 80% was impregnated with a perfluoro based ion exchange resin solution to produce a halogen-zinc cell diaphragm 25 μm thick with a dense texture.

The electrolyte diaphragm obtained in this fashion was tested and measured to determine its characteristics. Electrical resistance was 0.13 $\Omega \cdot cm^2$ (measured in 35% KOH $1KH_2$ a.c.). Virtually no swelling or other change was noted after immersion in 35% KOH for 2000 hours, demonstrating good product quality.

Merits of the Invention

The present invention outlined above offers an electrolyte diaphragm with improved mechanical strength and capable of a high degree of film thinning, that exhibits excellent characteristics in terms of dimensional stability, that has low electrical resistance in assocation with the aforementioned film thinning, and that has excleent coulomb efficiency, and is an invention that is exceedingly useful to industry.